

## Canaigre Investigations

### IX. Laboratory Tannage of Heavy Leather\*†

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#### ABSTRACT

Blocks of steer hide were tanned in the laboratory with canaigre extracts made by several methods. All the leathers produced were well tanned, firm, well filled, and of good appearance. Extracts made with water gave better penetration into the hide, and formed less sludge during tannage than those made with solutions of water and isopropyl alcohol or acetone. An extract made with water at 150° F. gave better tanning results than those made at either higher or lower temperatures.

#### INTRODUCTION

Final evaluation of a new tanning material requires a large-scale commercial tanning test. A sufficient amount of canaigre extract for such a test has not yet been made. However, sufficient extract was on hand to tan, on a laboratory-scale, several hides cut into blocks of suitable size. Although such a test is not equivalent to a large-scale test, it indicates the type and quality of leather which can be made and gives a comparison of the tanning properties of different types of extract.

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\*\*One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Administration, United States Department of Agriculture.

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## EXPERIMENTAL WORK

Two series of tanning tests were made. In the first series, two kinds of canaigre extracts were used; one was a liquid extract made by water extraction, and the other a powdered extract made by extraction with an 18 per cent solution of isopropyl alcohol in water.\* One tannage was made with each of these extracts. As there was an insufficient amount of the alcohol extract, a slight amount of similarly prepared extract with a somewhat higher purity was used during the last week of tannage. A third tannage was made with a blend of 40 per cent of the alcohol extract, 30 per cent of sulfited quebracho, and 30 per cent chestnut wood extract. A fourth tannage was a control tannage made with a blend of equal parts of quebracho and chestnut extracts. Each of the vats used held one side of leather cut into 15 by 12 inch blocks. Four hides, previously limed, unhaired, and delimed slightly, were cut into blocks of this size. Each hide served for two comparative tannages. Alternate blocks from each side were put into two vats so that each vat contained a mixture of right and left-hand pieces and each piece was matched by a piece in the other vat from a corresponding position on the other side of the animal. The weight of tanning liquor was about three times the weight of the wet white hide pieces.

Tannage was started in a liquor containing 0.5 per cent tannin. Every day one-third of the liquor was discarded, and enough settled, clear stock liquor added to raise the strength 2° barkometer over that of the preceding day. Each day for the first 10 days, the pH was adjusted to 4.5 by addition of lactic acid. During the first few days, there was a rapid raise in pH, caused by the lime in the hides and the lack of buffering material in the liquors, so that the actual pH of tanning ranged from about 5.5 in the tail liquor to 4.5 in the liquor after 10 days. For the remainder of the time, the pH was determined but unadjusted. Every few days, until the pieces were completely "struck through" by the tannin, cuts were made in pieces of comparative thickness and location to determine the rate of penetration of the tannin. The time of tannage was 6 weeks. The strength of the final liquors was 65° barkometer.

Four more tannages were included in the first series. The liquors for these tannages were the discarded liquors from the first tannages except for the fresh liquors used in the final week. They were started 1 week after the first four tannages. The amount and composition<sup>1</sup> of all fresh and discarded liquors from all tannages were determined and recorded.

This method of tannage is different from the countercurrent system used commercially, which could not be used in these tests because of shortage of materials. Although the laboratory system might have a slight advantage over the other because impurities are not accumulated, it is, on the whole,

\*Canaigre extracts prepared by extraction with water are subsequently referred to as water extracts; those prepared by extraction with a solution of isopropyl alcohol in water are referred to as alcohol extracts; the term solvent extract refers to an extract prepared by extraction with a solution of either isopropyl alcohol or acetone.

disadvantageous. In practice, the liquors are mellowed by contact with partly tanned leather and consequently are less astringent when applied to fresh hide. In addition, they accumulate buffer salts, so that it is possible to adjust the pH without sharp peaks and dips.

There was a fairly heavy growth of mold on the liquors. Although this was partly due to the method of tannage, apparently canaigre has more of a tendency to mold than do other tanning materials. There was less mold on the controls than on the canaigre tannages. A marked difference was noted in the sludge or deposit formed in the liquors. The amounts formed in the liquors prepared from water-extracted canaigre, the blend, or the control liquors were normal for usual tanning materials. In the solvent-extracted canaigre liquors, however, a heavy sludge formed. In these liquors, the apparent sapping each day was considerably more than in the other liquors, because in addition to what was taken up by the leathers, solids were lost by settling. Therefore, to maintain the strength of the solvent liquor, much more stock liquor was required than for the other tannages.

After tannage, the leathers were washed. A marked difference was noted between the pieces tanned with solvent extract and those of the other tannages. All the pieces were easily washed except the pieces tanned with the solvent extract, and they required vigorous scrubbing with a brush. The pieces were oiled lightly, dried, and weighed. They were then bleached, oiled and dried by the usual procedure at a commercial tannery, along with a pack of regular leather being given these treatments. They were pressed at the laboratory and conditioned at 73° F. and 50 per cent relative humidity, weighed and measured for thickness. Tensile strength was determined on a Tinius Olsen "Plastiversal" testing machine of 0-500 pounds capacity. Elongation was measured on the same machine at a load of 100 kilograms per centimeter width. Water absorption was measured by the method of Whitmore and Downing<sup>2</sup>. Shrinkage temperatures were determined by the Theis Shrinkage Tester, according to the specifications of the provisional method of the American Leather Chemists Association<sup>1</sup> (1942); no adjustment of the pH was necessary. Determinations of pH and chemical analyses were made by the official methods of this Association.

In the second series of tanning tests, eight types of canaigre extracts, prepared by Rieder et al.<sup>3</sup> were used. Five of these were prepared by water extraction—one at 112° F., one at 114°, one at 150°, one at 170°, and one at temperatures ranging from 175° on the tail to 115° on the head leach. Three extracts were prepared by extraction with solutions of organic solvents: one with an 18 per cent solution of isopropyl alcohol at 112° F.; one with a 10 per cent solution of isopropyl alcohol at 112° F.; and one with a 25 per cent solution of acetone at 80°. Another tanning test was made with an extract prepared by treating the 18 per cent alcohol extract with 3 per cent sodium sulfite on a total solids basis, to prevent formation of insoluble material.

Since smaller amounts of material were available for the second series of tests, than for the first series, they were made in battery jars each holding three 10.5 by 8 inch-pieces. A hide similar to those used in the first series of tests was cut into blocks of this size, and two blocks from the bend portion and one from the belly or shoulder portion were tanned in each jar. The distribution of pieces was such as to give fairly comparable results. The liquor-to-hide ratio was about the same as in the first series. The tanning method was, in general, the same as in the first series except that instead of increasing the barkometer strength of the liquors to a definite extent each day, stock liquors were added in amounts that gave the same addition of tannin to each vat. In these tests, mold growth was prevented by addition of a small amount of preservative (phenyl mercuric acetate).

As in the first series, a tendency for sludge formation was noted in the liquors from the solvent extracts and, to a smaller extent, in the liquors from the water extracts made at 170° F. and 175° F. Because of the small size of the vats used in this test, the comparatively vigorous rocking motion, and the mixing motion caused by removing the hide pieces, the liquors became well mixed before the sapped portion was taken off. Therefore, a large proportion of the sediment formed each day was removed and did not accumulate as it did in the first test, and as it would in actual tanning.

The leathers were weighed wet, after removal of superficial water with a towel. Since an opportunity became available to have these leathers finished in a tannery, in conformity with usual tannery practice, without an intermediate drying after tannage, they were handled in this manner. In this respect, they differed from the leathers in the first series, which were dried between tanning and finishing.

TABLE I  
Analyses of Extracts\*—First Series of Tanning Tests

	Total Solids %	Soluble Solids %	Insolubles %	Non tannin %	Tannin %	Purity Tannin Soluble Solids
Alcohol extract I	95.0	91.1	3.9	36.0	55.1	60.5
Alcohol extract II	96.1	87.6	8.5	29.6	58.0	66.2
Water extract	46.1	45.6	0.5	18.2	27.3	60.0
Blend	45.0	43.2	1.8	13.2	30.0	69.4
Control	50.7	48.3	2.4	11.7	36.6	75.7

\*Alcohol extract I was prepared by extraction with 18% isopropyl alcohol solution at 112–116° F.

Alcohol extract II was a composite of three extracts prepared by extracting (1) with 18% isopropyl alcohol-water, (2) with 15½% isopropyl alcohol-water, and (3) with 25% acetone-water mixtures.

Liquors from which alcohol extract II and the water extract were made were fermented to improve purity, but those used in preparing alcohol extract I were not fermented. Only slight amounts of extract II were used for strengthening liquors during the last week of tannage.

The blend consisted of 40% of the alcohol extract, 30% chestnut wood extract, and 30% quebracho extract.

The control was a blend of 50% quebracho extract and 50% chestnut wood extract.

## DATA AND CALCULATIONS

Table I shows the analyses of the extracts used in the first series of tanning tests. There is little significant difference in the analyses of the three canaigre extracts.

The time required for complete penetration of tannin through pieces of hide of equal thickness ( $\frac{1}{4}$ " ) was: in the first round, water-extract, 17 days; alcohol-extract, 20 days; blend of canaigre, chestnut, and quebracho, 19 days; and control, chestnut and quebracho, 16 days. In the second round, it was: water-canaigre, 20 days; alcohol-canaigre, 23 days; blend, 20 days; and control, 19 days.

Table II shows some data on yields and tannin consumption for the first series of tests. The yield figures are somewhat higher for the first round of the alcohol extract than for the other extracts. The tannin consumption reported is tannin either taken up by the leather or lost. It is calculated by determining the total tannin in the stock liquor used and subtracting from this figure the tannin discarded and that remaining in the liquors at the end of tannage. This figure divided by the grams of leather gives the tannin consumption per gram of leather tanned. If calculated on the basis of the rough dry leather, the tannin consumption is due to tannage alone; if calculated on the basis of the finished leather, it is due to tannage plus oils and loading materials. The tannin consumption for the first round of the alcohol-extract tannage was considerably higher than that for the other tannages. In the second round, there were only slight differences in the results obtained.

TABLE II  
Leather Yields and Tannin Consumption—First Series of Tanning Tests

	Leather Yields		Tanning Consumption per gram of leather	
	White Weight to Rough Dry Leather %	White Weight to Finished Leather %	Rough Dry Leather grams	Finished Leather grams
Water extract				
1st round	60.3	69.8	0.42	0.36
2d round	60.1	69.7	0.42	0.34
Alcohol extract				
1st round	63.2	73.2	0.57	0.50
2d round	61.5	69.3	0.42	0.34
Blend				
1st round	57.9	70.4	0.49	0.41
2d round	57.7	69.3	0.49	0.36
Control				
1st round	58.8	69.9	0.46	0.39
2d round	58.6	69.7	0.46	0.38

Some chemical and physical data on the leathers in the first series of tests are shown in Table III. Although the yield of the alcohol-extract leather (Table II) was higher than that of the water-extract leather, the combined tannin in the former leather was only 26.5 per cent as compared with 30.4 per cent in the latter leather. The higher yield was due to the larger amount of soluble matter—30.8 per cent—as compared with 23.7 per cent for the water-extract leather. The remaining data in the chemical analyses require no comment. They are normal for this type of leather. There are some variations in the data for tensile strength and water absorption. However, these methods are not sufficiently accurate for these variations to have appreciable significance.

TABLE III  
Chemical and Physical Data on Leather—First Series of Tanning Tests

	Water Extract		Alcohol Extract		Blend		Control	
	1st Round	2d Round	1st Round	2d Round	1st Round	2d Round	1st Round	2d Round
Oils and fats, %	4.2	6.4	5.7	7.0	6.1	8.0	5.1	5.8
Insoluble ash, %	0.3	0.3	0.4	0.3	0.4	0.4	0.4	0.4
Soluble matter, %	23.7	23.2	30.8	22.7	23.5	25.3	22.2	27.6
Hide substance, %	41.4	41.0	36.6	41.1	40.0	40.1	40.5	39.5
Combined tannin, %	30.4	29.1	26.5	28.9	30.0	26.2	31.8	26.7
Degree of tannage, %	73.4	70.9	72.4	70.3	75.0	65.3	78.5	67.6
Soluble nontannin, %	15.7	16.5	18.4	16.6	17.0	17.2	15.1	17.3
Soluble tannin, %	8.0	6.7	12.4	6.1	6.5	8.1	7.1	10.3
Total ash, %	5.6	5.4	5.7	5.4	6.3	5.9	5.8	5.5
Epsom salts, %	7.1	6.5	7.1	7.0	7.7	7.4	6.6	6.5
Glucose, %	3.8	3.8	4.8	4.4	5.0	4.6	5.0	5.1
pH,	3.1	3.8	3.0	3.1	3.3	3.9	3.9	3.4
Shrinkage temperature, C°	82	89	84	87	86	86	86	85
Tensile strength, lbs./sq. in.	4500	4440	4610	5550	3890	4960	5070	—
Elongation, %	19	20	18	18	21	18	16	—
Water absorption								
30 minutes (A), %	24	25	35	27	37	40	48	—
24 hours (B), %	44	50	51	50	54	56	60	—
Ratio A/bx 100	55	50	70	54	69	72	80	—

Table IV gives the analyses of the extracts used in the second series of tanning tests. The most significant data are the figures on purity. The comparatively high purities of some of the extracts were due to a fermentation process, which reduced the amount of nontannins.

The time taken for complete penetration of tannin through pieces of hide of equal thickness in the second test was: for the water extracts prepared at 112° F., 23 days; at 114°, 22 days; at 150°, 22 days; at 170°, 23 days; and at 115–175°, 24 days. For the solvent extracts, the time was: 18 per cent alcohol,

28 days; 10 per cent alcohol, 24 days; acetone, 26 days, and sulfited liquor, 16 days.

TABLE IV  
Analyses of Extracts—Second Series of Tanning Tests

	Total Solids %	Soluble Solids %	Insolubles %	None-tannin %	Tannin %	Purity* Soluble Tannin Solids
Water, 112° F.	95.8	94.9	0.9	40.4	54.5	57.4
Water, 114° F.	96.4	95.1	1.3	35.1	60.0	63.1
Water, 150° F.	96.0	92.3	3.7	28.9	63.4	68.7
Water, 170° F.	95.1	92.2	2.9	34.7	57.5	62.4
Water, 115-175° F.	96.1	94.0	2.1	33.2	60.8	64.6
18% isopropyl alcohol 112° F.	96.9	93.9	3.0	28.7	65.3	69.5
10% isopropyl alcohol, 112° F.	96.4	95.0	1.4	32.3	62.7	66.0
25% acetone, 80° F.	94.9	93.6	1.3	35.2	58.4	62.4

\*The higher purities of extracts 2-7 are due to the fact that their sugars were removed by fermentation, thus lowering the nontannins.

Table V gives the yields and tannin consumption of the leathers in the second series of tests. The rough weights of the leather are the wet weights instead of the dry weights as in the first series. Only slight differences in tannin consumption are shown. However, the system used in the two tannages was different. In the first series, the strength of the liquors was maintained at a definite figure, irrespective of losses, but in the second series, a definite amount of tannin was added to each vat without regard to the final strength. In the second series, differences in the tannin consumption were

TABLE V  
Leather Yields and Tannin Consumption—Second Series of Tanning Tests

	Leather Yields		Tannin Consumption per gram of Leather	
	White Weight to Wet Rough Leather %	White Weight to finished Leather %	Rough Wet Leather grams	Finished Leather grams
Water, 112° F.	114.0	75.4	0.13	0.39
Water, 114° F.	115.8	76.3	0.12	0.36
Water, 150° F.	120.2	89.2	0.14	0.38
Water, 170° F.	113.7	74.5	0.12	0.37
Water, 115°-175° F.	115.3	77.6	0.12	0.34
18% isopropyl alcohol, 112° F.	112.7	74.4	0.15	0.40
10% isopropyl alcohol, 112° F.	113.2	82.9	0.13	0.36
25% acetone, 80° F.	112.9	73.6	0.12	0.37
Sulfited liquor	114.8	72.6	0.12	0.37

TABLE VI

	Extract Prepared by Water Extraction at				Extract Prepared by Water-Solvent Extraction				
	112°F.	114°F.	150°F.	170°F.	115-175°F.	18% propyl Alcohol	10% Iso- Alcohol	25% Acetone	Sulfited
Oils and fats, %	5.2	5.0	5.3	5.8	5.3	4.3	4.1	4.1	6.5
Insoluble ash, %	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2
Soluble matter, %	30.1	32.7	31.9	30.4	32.7	28.4	30.8	27.8	30.5
Hide substance, %	37.5	35.4	33.3	38.1	34.4	38.1	36.5	39.6	38.0
Combined tannin, %	26.9	26.7	29.3	25.5	27.4	29.0	28.3	28.3	24.8
Degree of tannage, %	71.8	75.2	87.7	66.9	79.7	76.1	77.5	71.5	65.3
Soluble nontannin, %	20.8	21.7	21.5	20.0	22.5	18.1	20.3	18.1	20.5
Soluble tannin, %	9.3	11.0	10.4	10.4	10.2	10.3	10.5	9.7	10.0
Total ash, %	5.8	6.5	6.5	6.1	6.9	5.3	6.1	4.8	5.7
Epsom salts, %	7.4	7.6	7.7	7.5	8.2	7.1	7.3	6.5	7.1
Glucose, %	7.6	7.8	7.4	7.1	8.5	6.4	7.2	6.3	7.8
pH	3.6	3.6	3.5	3.6	3.6	3.6	3.6	3.8	3.7
Shrinkage temperature, C°	84	86	84	85	85	86	82	85	83
Tensile strength, lbs. / sq. in.	3500	3300	3200	3500	2600	3000	2700	3100	3200
Elongation, %	17	21	14	17	23	14	23	17	20
Water absorption									
30 minutes (A), %	44	40	49	47	47	37	48	51	39
24 hours (B), %	66	66	66	62	69	58	70	64	67
Ration A/B x 100	67	61	74	76	68	64	68	80	58



decreased or eliminated. Any differences should be shown in the yield figures—white weight to rough weight. On the whole, these figures are lower for the solvent-extract leathers than for the water-extract leathers, especially at medium or low temperatures. The most striking point in Table V is the high yield obtained with the 150° water extract, both on the rough and finished leather. The high yield obtained by the 10 per cent alcohol leather in the finished state is interesting, but as it was not confirmed by a corresponding high yield in the rough state, it must be considered as due to increase added in the oil wheel and of no particular significance in the actual tanning. In comparing Table V with Table II, it must be kept in mind that because of different methods of finishing, the weights of the dry rough leather are used in Table II, whereas in Table V the weights of the wet leather are used.

Table VI gives the chemical and physical data on the leathers in the second series of tests. As in the first series, most of the data require no comment, as they are normal for this type of leather. The most striking figure is the high degree of tannage, 87.7, for the 150° water-extract tannage, confirming the figures on yields in Table V.

#### DISCUSSION

All leathers produced were satisfactory. They were firm, full, well-filled, and of good appearance. All canaigre extracts used by themselves gave good tannages, and a blend of canaigre extract with sulfited quebracho and chestnut extracts also gave good results.

One objection to canaigre is a tendency to mold. This may be prevented by the use of a small amount of preservative, which would have the disadvantage of preventing acid formation. However, acid formation in canaigre liquors is slight, and it would probably be more advantageous to add the required amount of acid rather than to depend upon fermentation. As canaigre extract would probably be used in blends with other materials, the bad effects of mold growth would be lessened, especially with the usual countercurrent method of tanning.

The penetration of tannin into the hide is more rapid with liquors made from water extracts than with liquors made from solvent extracts. In addition to delaying the tannage, slower penetration of the tannin has another effect. If the cut edges of the solvent-extract tanned leather are examined, dark layers or streaks are noticed, showing uneven tannage. Although this defect would almost certainly not occur in the countercurrent system of tannage used in commercial practice, it indicates a difference in tanning properties between the two types of extracts.

The higher figures on yield and degree of tannage in Tables V and VI show clearly that the extract giving the best tanned leather was that prepared by extraction with water at 150° F. The extract prepared with acetone was inferior to those prepared with isopropyl alcohol. However, as the 18 per cent

alcohol extract was inferior to the 10 per cent alcohol extract, possibly the inferiority of the 25 per cent acetone extract was due more to the amount than to the nature of the solvent. The quality of the leather produced indicates that in solvent extraction the amount of solvent used should be kept to a minimum.

Sulfiting the extract improved penetration and color, but as expected, lowered the yield.

The question of sludge formation is important. The resulting loss of tannin necessitates a greater amount of tannin to produce the same amount of leather, as in the first round of the first series, or results in the production of a smaller amount of leather from the same amount of tannin, as shown in the yields of white weight to wet rough leather in the second series of tests. The results in the second round of the first series indicate that these liquors became stabilized by precipitation of sediment in the first round, and after this there was no further excessive deposition. In leathers tanned with the sludge-producing extracts, analysis showed that the tannin was less thoroughly combined than with other tannages. Furthermore, the sludge would require an extra process of scouring the leather. At present any comparison of cost of extracts produced by solvent extraction and those produced by water extraction only would be premature. However, it is certain that for solvent extraction to compare favorably with water extraction, greater recovery of tannin is necessary. Further work on the solvent extraction process is necessary to determine whether the extra tannin recovered is of advantage or whether it is lost during tannage.

#### CONCLUSIONS

Satisfactory leathers have been made from canaigre extracts prepared in various ways. Extracts prepared by water extraction gave better results than those prepared with a mixture of water and organic solvents. The best tanning results were obtained with an extract prepared with water at 150°F.

#### ACKNOWLEDGMENTS

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## DISCUSSION

WALLACE WINDUS: The significance of this research from the standpoint of national self-sufficiency in case of an emergency is apparent to all. The problem itself is particularly suitable for a government research laboratory, because it is of necessity a long-range project which requires patience and adequate financing.

Those of us who have visited any one of these Regional Research Laboratories know that the engineering facilities are impressive, indeed. And we are glad to be constantly reassured that the staff is definitely cost-conscious.

I have a few questions to lead off the discussion. I got the impression from Mr. Rogers' paper that the engineering staff has not yet decided on any one method of extraction. This paper is in the nature of a progress report, and I understand that further work will be done to decide on the most suitable extraction procedure from the standpoint of whether solvent or water and organic solvent combination. I would like to know if I am correct in that impression.

I also wonder about the amount of starch that still remains in the extract—whether there is a significant amount in the final extract and whether it has any disadvantages, if it is present.

It did appeal to me that the use of fermentation might not be necessary from a practical standpoint, since the purity is 58 per cent without fermentation, whereas it is only 69 per cent after fermentation, and some tanners might feel that the presence of fermentable sugars was desirable.

I was curious about the degree of tannage, but my question on that was answered. It is certainly adequate and satisfactory.

I would like to know something about the stability of the tannage in comparison with other tannages—whether the linkage of the canaigre tanning material with the protein is as strong, approximately, as with other vegetable materials.

MR. BEEBE: The extract was prepared in such a way as to eliminate the starch. Tests have shown that the amount of starch in the extract is insignificant.

As far as economy of the organic solvents as compared with water, that is still being worked on by the engineering Division and has not yet been settled. It is an engineering question. The cost of organic solvents is, of course, greater than water, but on the other hand, you get out more tannin. Whether one will balance the other or not is a question not yet decided.

We have not made any particular tests on the stability of the tannage yet.

WINDUS: I am thinking particularly of washing. Is it stable to washing and not readily washed out?

BEEBE: It is stable. In working with canaigre extract, I would say that it is an average tannage. It does not have any particular advantage or disadvantage.

vantage. It can be used as a blend with other materials. Particularly I would suggest that canaigre be used as most other tanning materials—blended with other tanning materials, such as quebracho and chestnut. You can use up to 40 per cent in blends.

We have not yet got to the point where we are producing the extract in high enough quantities to be used in a commercial tanning test, but we do expect to have a few hundred pounds in a little while, so that we can distribute a few pounds to anybody who is interested in working with that much.

MR. HILBERT: What is the percentage of starch in the original material that you have to remove?

ROGERS: In the dry, moisture-free roots the starch content will vary from around 25 per cent to 40 per cent.

DR. TU: I would like to know about the economic angle of a plantation of canaigre.

ROGERS: We have between twenty and thirty acres in canaigre, and expect to harvest about fourteen acres this summer. We anticipate that the yield will be in the neighborhood of 150 to 200 tons of fresh roots. We do not have specific data as to the cost of production. However, the canaigre can be planted with drills or planting machines in a manner similar to that used for other seeded crops, and the matured roots can be harvested with potato digging equipment. We see no reason why it should not be economically feasible. We hope to get cost data on some of that processing this year after the harvesting.

TU: How about the other parts of the plant? Do you find some other use for the other materials in the roots?

ROGERS: We are working on the utilization of both the starch and the sugar. At present, our fermentation process utilizes bacteria that remove sugars and raise the purity of the liquors, but the products of fermentation are not easily recovered. Studies of other fermentation procedures are underway which may produce a better by-product. The starch can be hydrolyzed and fermented. We hope to utilize both of these materials.

TU: Did you state that you get 37 per cent average tannin content from the roots?

ROGERS: Two different strains of roots have been observed so far. One type has yellow interiors and the tannin content varies from about 20 per cent to 25 per cent on a moisture-free basis. The other type of root has a reddish interior and its tannin content varies from 30 per cent up to as high as 54 per cent on a moisture-free basis. A further survey of wild plants is being made which may disclose other strains with different properties.

DR. BUECHLER: A number of years back, Mr. Roddy showed that tanning could be done with a solvent system. I wonder if Mr. Beebe has done work to see how well this material would tan in a solvent system?

BEEBE: We have not made any tests on solvent tanning.

BUECHLER: From the viewpoint of a national emergency, where it would be desirable to have a source of tannin in this country, it might be possible, instead of trying to get a water-soluble product, to sell your solvent extract of canaigre for solvent tannage. That would bring a lot of problems to the tanner, because he would have to have a solvent recovery system. However, he would save a lot of time in processing, because solvent tannage is so much faster. It would be a possibility, I think, to keep in mind.

BEEBE: I don't believe that solvent tannage has as yet proved commercially successful. You can tan with solvents very rapidly, but whether you can get as high a yield of leather, I don't know. In time of a national emergency, there might be difficulty in obtaining solvents.

ROGERS: If any of you are interested in seeing heavy leather that has been tanned with canaigre extract we have some of it here.

WINDUS: In view of this discussion on the solvent tannage, if I may make one comment: I think it is very interesting as a theoretical laboratory procedure to study the mechanism of tanning, assuming that the reaction is analogous to what takes place in a water medium, of course. It is followed by water, so probably the mechanism of the tanning ends up the same, but I do not feel that it is a practical method of tanning. I don't think you will find tanners willing to consider all the expense and difficulties involved. A practical tanning agent to me must be water soluble.

DR. FLINN: Mr. Beebe gave tables showing three leathers tanned with extracts that were leached at three different temperatures—115, 150, and 180° F. Would the yield indicate that the one leached at 150° was significantly higher? Would you give an explanation for that?

BEEBE: I believe that the explanation is that at temperatures lower than 150°, there is insufficient extraction of tannin, while at higher temperatures there is interference by starch.

FLINN: Wouldn't that imply that since you had extracts leached at three different temperatures you were using extracts for tanning that had the chemical structure of the tannin molecule altered?

BEEBE: It may be possible. I don't have enough information to say that.